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Selenium Transformations in Ponded Sediments

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ABSTRACT

Features of the sediment contamination process that occurred during disposal of seleniferous agricultural drainage waters at Kesterson Reservoir (California) were simulated in the laboratory. Selenium was introduced by ponding 3.0 m*M* solutions of Se(VI) over previously uncontaminated soils. Analyses of soil waters and ponded waters with conventional laboratory methods [hydride-generation atomic absorption spectrometry (HGAAS) and redox electrodes] and with x-ray absorption spectroscopy (XAS) measurements on sediment and water samples provided direct Se speciation of the dominant valence states. The XAS demonstrated that Se in a contaminated sediment from Kesterson Reservoir occurs primarily as the red, monoclinic elemental form. Selenium(VI) reduction to Se(IV) and removal of both species from the aqueous phases (ponded and pore waters) was observed with HGAAS. Reduction of Se(VI) to Se(0) in the sediments was confirmed with XAS. The XAS on all shallow sediments at the end of the ponding period (48 to 51 d) demonstrated that 99 ± 5% of the Se occurred as Se(0). Rapid reoxidation of Se(0) was observed in some of the previously ponded sediments. About 60% of the Se inventory was reoxidized to a mixture of Se(IV) and Se(VI) in unamended sediments within 2 d after sampling. Selenium in sediments that were amended with organic matter remained in the Se(0) state during this short period.

THE IMPORTANCE of Se as a naturally occurring, potentially toxic trace element in various natural and human-affected environments has received considerable public and scientific attention during the past 60 yr (e.g., Anderson et al., 1961; Rosenfeld and Beath, 1964; Sharma and Singh, 1983; Frankenberger and Benson, 1994). Understanding which of the various possible oxidation states and coordination structures prevail under various conditions is essential since these factors control Se mobility, bioavailability, and toxicity (Geering et al., 1968; Elrashidi et al., 1987). Selenate, SeO_4^{2-}, containing Se(VI), is the stable water-soluble (hence mobile) species under oxidizing conditions. Selenite, SeO_3^{2-}, containing Se(IV), is stable under slightly suboxic conditions. Adsorption of $HSeO_3^-$ and SeO_3^{2-} onto surfaces of soils and specific minerals has received considerable attention (e.g., Hingston et al., 1971; Rajan and Watkinson, 1976; Hamdy and Gissel-Nielsen, 1977; Balistrieri and Chao, 1987; Bar-Yosef and Meek, 1987; Neal et al., 1987; Hayes et al., 1987; Barrow and Whelan, 1989; Christensen et al., 1989). Under more reducing conditions, several different allotropes of elemental Se become stable (Greenwood and Earnshaw, 1984). While the importance of microorganisms in mediating Se reduction transformations in soils has been well established (e.g., Doran, 1982; Zehr and Oremland, 1987; Oremland et al., 1989; Macy et al., 1989; Oremland et al., 1990; Lortie et al., 1992; Macy et al., 1993), very little information on microbial Se oxidation is available (Sarathchandra and Watkinson, 1981). The contamination of Kesterson Reservoir (Merced County, California) with seleniferous agricultural drainage waters, and resulting wildlife mortalities, impaired reproduction, and deformities accompanying it, illustrates the need for reliable speciation information to understand Se transport, immobilization, bioavailability, and toxicity (Ohlendorf, 1989; Weres et al., 1989a; Benson et al., 1991; White et al., 1991; Tokunaga et al., 1991; Zawislanski et al., 1992, Tokunaga et al., 1994a).

Although the previously cited literature indicates a long period of appreciation for the controls that valence and coordination environment place on Se cycling in the environment, relatively little direct information of this type is available. In particular, studies of Se in soil and groundwater systems have, to date, only provided direct speciation in the aqueous and gaseous phases. In soils, Se associated with these phases commonly comprises a small fraction of the total soil Se inventory. In the contaminated sediments of Kesterson Reservoir, this fraction is largely accounted for by Se(VI) in soil waters and amounts to only ≈10% of the total Se inventory. The occurrence of Se(IV) and Se(0) in the remaining adsorbed and solid phases of Se has been inferred from a variety of selective extraction techniques (Presser and Barnes, 1985; Weres et al., 1989a; Gilliom, 1989; Benson et al., 1991; White et al., 1991; Lipton, 1991; Tokunaga et al., 1991). However, interpreting the data from such extractions may be problematic since the samples of interest are subjected to conditions that are substantially different from those of the natural field environment. In addition to uncertainties that may arise about valence state, extraction methods cannot distinguish adsorption from precipitation (Sposito, 1984). Thus, ≈90% of the Se inventory at Kesterson Reservoir requires analyses that will supplement previous characterizations based upon extraction methods. Such issues are not specific to Se, since they may arise in the use of sequential extraction methods for many other chemical constituents (Kheboian and Bauer, 1987; Gruebel et al., 1988; Beckett, 1989; Belzile et al., 1989; Qiang et al., 1994).

Synchrotron-based XAS methods have proven effective in obtaining information on local structural and electronic environments for a wide range of elements in model systems of geochemical interest (Brown et al., 1988; Brown and Parks, 1989; Fendorf et al., 1994; Brown et al., 1995). Studies of adsorption have included adsorbates such as Cr, Co, As, Se, Pb, and U and adsorbents such as rutile, quartz, oxides and hydrous

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Abbreviations: HGAAS, hydride-generation atomic absorption spectrometry; XAS, x-ray absorption spectroscopy; EXAFS, extended x-ray absorption fine structure; XANES, x-ray absorption near edge structure; XRF, x-ray fluorescence spectrometry; PVC, polyvinyl chloride; ICP, inductively coupled plasma spectrometry.

oxides of Fe and Al, and aluminosilicate clays (Hayes et al., 1987; Brown et al., 1989; Chisholm-Brause et al., 1990a, 1990b; Bajt et al., 1993; Manceau and Charlet, 1994). Note that these systems include important trace element soil contaminants and soil minerals. Extended x-ray absorption fine structure (EXAFS) studies provided the first direct evidence for inner-sphere, bidentate adsorption of Se(IV) on geothite (Hayes et al., 1987). There is also the suggestion that Se(VI) forms inner-sphere complexes on goethite and hydrous ferric oxide based on EXAFS measurements (Manceau and Charlet, 1994). The XAS has also recently been used to determine the nature of Se(VI) incorporation into calcite (Reeder et al., 1994). Valence of elements susceptible to oxidation and reduction may be obtained through their x-ray absorption near-edge structure (XANES) (Waychunas et al., 1983; Wong et al., 1984; George and Gorbaty, 1989; Bajt et al., 1993; Sutton et al., 1993). For a given element, different valences may be discerned by characteristic shifts in energies of the absorption edge that reflect the valence-dependence of core electron binding energies. With many elements, XAS techniques are often applicable to undisturbed bulk samples at atmospheric pressure and room temperature. Applications of XAS in environmental samples have provided direct speciation of many elements including U (Bertsch et al., 1994), Mn (Schulze et al., 1995), and S (George et al., 1991; Vairavamurthy et al., 1994). The XANES region is sensitive to both the valence state and the local atomic environment of the absorbing atom, thus making it a particularly sensitive indicator of the species present. Quantitative speciation of mixtures of two or more occurrences of the same element can also be achieved (George et al., 1991; Vairavamurthy et al., 1994; Pickering et al., 1995). Furthermore, for dilute systems, the XANES has an advantage over EXAFS in terms of signal-to-noise, as it encompasses a much smaller energy range and has more intense features. This permits more rapid acquisition of XANES spectra relative to EXAFS. All of these attributes make XAS (especially XANES) well suited for understanding states of a range of elements under conditions typical of the terrestrial environment. These previous, as well as ongoing, studies provide the foundation from which XAS methods may be directed towards understanding the nature of trace element contaminants in soils and sediments.

In view of the aforementioned considerations, a study of Se-contaminated soils that included XAS was initiated. After collecting x-ray absorption spectra of various model Se compounds, XAS was used to speciate Se in samples collected from Kesterson Reservoir and to directly monitor Se reduction in laboratory columns. The column experiment was designed to simulate some of the major factors controlling Se transformations during disposal of seleniferous drain waters at Kesterson Reservoir. In addition to analyses with XAS, Se in these ponded sediment columns was characterized with HGAAS, ICP, and conventional XRF. Redox potential measurements within ponded waters and sediments were also obtained. Details of the XAS analyses have been presented elsewhere (Pickering et al., 1994, 1995).

MATERIALS AND METHODS

The Kesterson Reservoir soils analyzed by XAS were collected from the northern region of Evaporation Pond #4, in an area formerly vegetated with cattail (*Typha latifolia* L.). The soils collected from the 0- to 50-mm and 50- to 150-mm depth intervals will be referred to as the 25- and 100-mm depth samples respectively. These two depth intervals had total Se concentrations of 344 ± 17 and 41 ± 2 mg kg^{-1}, respectively. Total Se concentrations in solid samples were determined by conventional energy-dispersive x-ray fluorescence spectrometry (XRF; Giauque et al., 1976). Note that the Se concentrations in these samples are considerably higher than average from Kesterson Reservoir. At the end of the period of Se input into Kesterson (1986), the average surface soil Se concentration was ≈ 10 mg kg^{-1}. We selected both field and laboratory samples with highly elevated Se concentrations to assure rapid collection of spectra with reasonable signal-to-noise ratios.

Laboratory soil columns were designed to study Se reduction within sediments following ponding with seleniferous waters. Soils for these columns were collected from Kesterson National Wildlife Refuge, in an area with no previous history of exposure to seleniferous waters. The sampling site, 200 m east of Kesterson Reservoir, is mapped as a Turlock sandy loam (fine loamy, mixed, thermic Albic Natraqualf), the predominant soil series found within Kesterson Reservoir (Nazar, 1989). These soils have developed along the western San Joaquin Valley basin rim, on nonseleniferous alluvium derived primarily from Sierran granite. The total Se concentrations in the sampled soil was <0.5 mg kg^{-1}. Vegetation at the sampling site consisted of a mixture of introduced annual grasses [*Hordeum* ssp., soft chess (*Bromus mollis* L.)] and salt-tolerant native species (coastal saltgrass [*Distichlis spicata* (L.) E. Greene], *Frankenia grandifolia*). Soils collected from the surface down to a depth of 150 mm were broken up to pass through a 4.75-mm sieve under field-moist conditions. The homogenized soils were then packed (while still at a field-moist water content of 0.178 kg kg^{-1}) in a series of 10-mm layers to a depth of 100 mm in four PVC columns (76.5 mm diameter) and to an equivalent dry bulk density of 1.28 Mg m^{-3} (Fig. 1). Initial values of total porosity and water-filled porosity were 0.52 and 0.23, respectively. The PVC columns had sealed bases and were sufficiently tall to permit ponding of waters above the soils. Platinum wire redox probes were embedded at depths of 0, 10, 50, and 90 mm below the soil surface. An additional Pt electrode was suspended above the soil surface in the ponded water within each column. The insulated leads from the Pt electrodes extended upwards above the water surface to terminals along the upper column exteriors. A calomel reference electrode was dipped just below the pond surfaces during measurements. Redox potentials were measured at hourly intervals during initial stages of the experiment. Calibrations of the Pt electrodes that were suspended in the ponded waters and at the sediment surface were rechecked at the end of the experiment and showed no significant drift. The frequency of these measurements was decreased during later stages of the experiment. The organic matter content of the soil was 1.0 ± 0.2%, as determined by the Walkley-Black method (Nelson and Sommers, 1982). Two of the columns were amended with cuttings of soft chess leaves and stems, which were mixed into the uppermost 30 mm of soil, to permit observation of possible influences of decomposing vegetation. The mass of organic matter added in this manner amounted to an air-dry equivalent of 0.2 kg m^{-2} (1.03 g per column), which corresponds to a typical quantity of annual grass biomass produced in the field site. Soil water samplers were embedded at 25 and

75 mm below the soil surface in one unamended and one organic matter amended soil column. These samplers were similar in design to that described in Tokunaga (1992), except that a smaller ceramic tip (7 mm diameter, 10 mm length, 0.2 mL pore volume) was used.

Waters with an initial Se concentration of 240 g m^{-3} (3.0 m*M*) were ponded over these previously uncontaminated soils. These initial aqueous Se concentrations were ≈ 10^3 times higher than typical values observed in the drain waters ponded at Kesterson Reservoir. As with the field samples, laboratory experiments were conducted with elevated Se concentrations to assure collection of spectra with low noise. Selenium was added to the laboratory solution as 2.94 m*M* Se(VI) (from Na_2SeO_4) and 0.06 m*M* Se(IV) (From $NaSeO_3$). This ratio of Se(VI) to Se(IV) was representative of typical agricultural drain waters that contaminated Kesterson Reservoir. Analyses of Se in ponded waters and soil waters were routinely performed by HGAAS (Weres et al., 1989b). Occasional total solution Se analyses were also performed by ICP. The major ion composition of the laboratory solution resembled that of the agricultural drain waters as well, being dominated by Na^+, SO_4^{2-}, and Cl^-, and was similar to that reported in Poister and Tokunaga (1992). Ponding with seleniferous water was established by dispensing 550 mL of solution over the soil surface during about a 1-min interval. This volume corresponded to an equivalent water column 120 mm deep. Upon dispensing the solutions, each column contained an initial ponding depth of 90 ± 3 mm, indicating that the soil profiles were close to water saturated (101 ± 10%). Some trapped air was expected to persist, especially towards the bottoms of these soil columns, because of the flooding procedure and the unvented bottom boundary.

Ponded waters in columns were disturbed as little as possible, in an attempt to discern the development of gradients in Se concentrations and speciation within the static water columns. Samples of ponded waters were collected at two depths; one at ≈ 7 mm below the water–air interface and a second sample at ≈ 10 mm above the sediment–water interface, via 1 mm i.d. plastic tubing attached to a syringe. Solution sample masses were kept small, ranging from 50 to 200 mg, to minimize disturbances to columns. Pond water sampling intervals ranged from daily (initially) up to 14 d towards the end of the ponded phase. Sediment pore water samples were also collected during the 48- to 51-d ponding period. Under ponded conditions, the empty samplers were sealed with initial pressures at or slightly above local atmospheric pressure ($\Delta P < +1.0$ kPa) to keep sample volumes small. Collected pore water samples were in the range of 1 to 3 g. Dilutions of both the pond and pore water samples were performed gravimetrically (1 mg resolution) prior to analyses. Under ponded conditions, a slightly vented lid was placed on each column top to minimize loss of any Se microbiologically converted into volatile forms (Reamer and Zoller, 1980; Zieve and Peterson, 1981; Thompson-Eagle and Frankenberger, 1989), as well as to minimize evaporative water losses. A beaker containing alkaline H_2O_2 solution (Weres et al., 1989b) was suspended in the headspace over each of the columns to trap volatilized Se. The column lids were periodically removed during exchange of peroxide traps. Alkaline H_2O_2 solutions for collection of volatilized Se were exchanged at ≈12-h intervals. During initial stages of the experiment, daily volatile Se samples were collected. Sampling for volatile Se was later scaled back to less frequent intervals.

Model compounds for XAS analyses of various selenium species were prepared primarily from their reagent-grade chemicals, diluted in either a BN powder or in an aqueous solution. Details of sample preparation methods are presented in Pickering et al. (1994, 1995). Sediment samples for XAS analyses were collected by vertically coring from the surface.

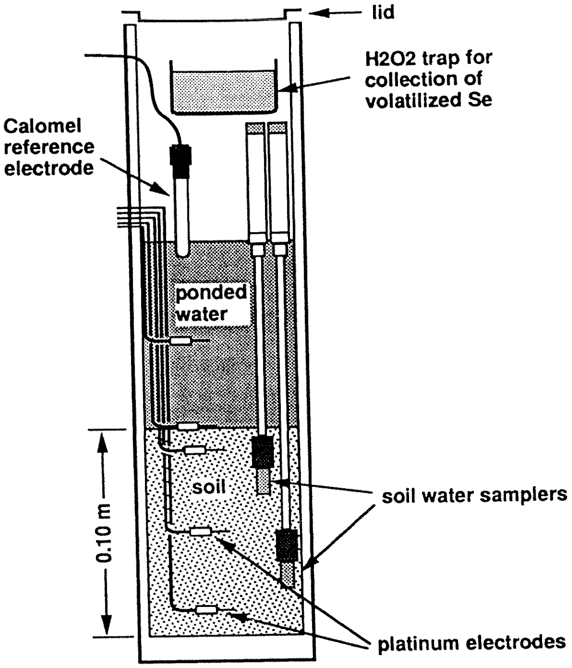
lid
H2O2 trap for collection of volatilized Se
Calomel reference electrode
ponded water
soil
0.10 m
soil water samplers
platinum electrodes

Fig. 1. Laboratory column design for ponding seleniferous waters over sediments.

For collection of a sample, a thin-walled stainless steel tube with a sharpened cutting edge was pushed (underwater) 30 mm into the sediment and pulled back to the surface while a slight vacuum was applied to the upper end of the tube. The sample was then quickly extruded and subcored to retain only the interior volume of the original core. The subcore sample was then pressed into a Mylar-backed, Teflon sample frame and sealed with a front window of Mylar tape. Most XAS analyses on wet sediments were conducted within 24 h of sampling. Samples obtained at the end of the pond period were analyzed as late as 70 h after collection to observe potential short-term changes in speciation arising from preservation methods. These latter samples were either (i) immediately sealed in Mylar-Teflon frames stored in N_2, (ii) immediately sealed in Mylar-Teflon frames stored in air, or (iii) air dried, then sealed into Mylar-Teflon frames. After collection of the final samples under ponded conditions, surface waters were removed and columns were air dried. Upon drying, each column was vertically sectioned for analysis of total Se by XRF.

Selenium K-edge XAS data were collected at the Stanford Synchrotron Radiation Laboratory. Experiments were performed at Stations 4-2 and 4-3, with Si(220) double crystal monochromators, upstream vertical apertures of 1 mm, and no focusing optics. Rejection of higher-order harmonics was achieved by detuning the monochromator to reduce beam flux by 50%. Spectra were collected in transmittance with N_2- and Ar-filled ion chambers whenever possible to avoid fluorescence thickness effects (self-absorption), and transmittance was used for all the model powders and solutions and for one of the soil samples. For samples that were too dilute to be run in transmittance, the spectra were recorded in fluorescence by monitoring the Se K_α fluorescence with a Canberra 13-element germanium detector. In this case, to minimize distortions in the windowed fluorescence signal due to electronic dead times (such distortions in the total incoming signal were negligible), the maximum total incoming count rate was maintained below 50 000 counts per second for all elements at all points in the spectra. Furthermore, for samples of intermediate Se concentration for which the transmittance signal was insufficient but the edge jump in the total signal was observed to be a substantial change, the total (i.e., nondispersive) signal was used instead of the windowed fluorescence counts. The spectrum of (gray, hexagonal) elemental Se was collected simultaneously with each data set as an energy calibrant, with the first inflection of its absorption edge taken to be 12 658 eV.

Data reduction was carried out with the programs PROCESS and DATFIT of the EXAFSPAK suite of programs. These programs for analysis of x-ray absorption spectra were written by Dr. Graham N. George of the Stanford Synchrotron Radiation Laboratory and are available from him on request. A background function was fitted to the pre-edge region and extrapolated through the entire energy range, and the function was subtracted from the spectrum. For transmittance data, this function was typically a first-order polynomial, and in the case of the germanium detector data, this was a Gaussian function to model the intensity of the scatter peak falling within the single channel analyzer window of the fluorescence counts. A stiff spline function was then fitted through the region above the edge, and the spectrum was normalized to the value of the spline at 12 690 eV. A Gaussian-smoothed second derivative of the edge was calculated with a 2-eV width and a third order polynomial.

X-ray absorption edge spectra were fitted to obtain quantitative speciation information with the program DATFIT. The method is based on the assumption that, for a sample containing more than one Se species, the resulting XAS spectrum will be the sum of spectra of pure components, the fractional contributions being directly proportional to the respective atomic concentrations in the sample. This assumption is good providing the samples are homogeneous with finely divided particles and that there are no distortions due to self absorption or other effects. In the fitting procedure, linear combinations of selected model compound spectra are compared with the unknown spectrum and scale factors for the individual components are refined in a least-squares optimization until the best fit is obtained. Optionally, a small energy offset is also minimized, although in this work, it was always observed to be <0.3 eV. We generally proceeded with the fits by testing different model compounds to find those that gave the best fit and then with the best components, refining the energy offset last of all. Independent fits were also carried out on the second derivative spectra using derivatives of model compounds, and the results of these were compared with those of the edge. In all the best fits, the edge and derivative spectra fits gave very comparable results.

A good fit was judged so by a number of criteria. First of all, a good relative R-factor, based on the sums of squares is sought, which will also be reflected in a visually good match between the observed and calculated spectra. The R-factor is useful for comparing fits of the same unknown to different models; however, in comparing fits of different unknown spectra, the R-factor reflects not only how good the model is but also how noisy the spectrum is. Another measure of the goodness of fit is the sum of the spectrum components, which, since the spectra are all normalized, should be unity for a perfect fit. The derivative spectrum is found to be especially sensitive to variations in this value. A final check on the quality of the fit is how similar the results of the independent edge and derivative fits are. For a good fit, they are expected to be identical; for poorer fits, much discrepancy is often found in the percentage values obtained. The accuracy (i.e., degree to which the answer obtained agrees with reality) of the quantitative speciation values obtained by this edge-fitting method will depend on many parameters, including the signal to noise of the data, the precision of the calibration, whether or not the data are free from artifacts such as fluorescence distortion effects, and the correct choice of standards. Assuming that the standards have been correctly chosen and that distortion effects are negligible, it is assumed from prior work on control aqueous selenite/selenate solution mixtures (Pickering et al, 1995) that the accuracy is ±5%.

RESULTS AND DISCUSSION

A comparison of the Se x-ray K-absorption edge spectra of aqueous and polycrystalline SeO_3^{2-} and SeO_4^{2-} and of two different allotropes of elemental Se are shown in Fig. 2. Selenium spectra for other standard compounds

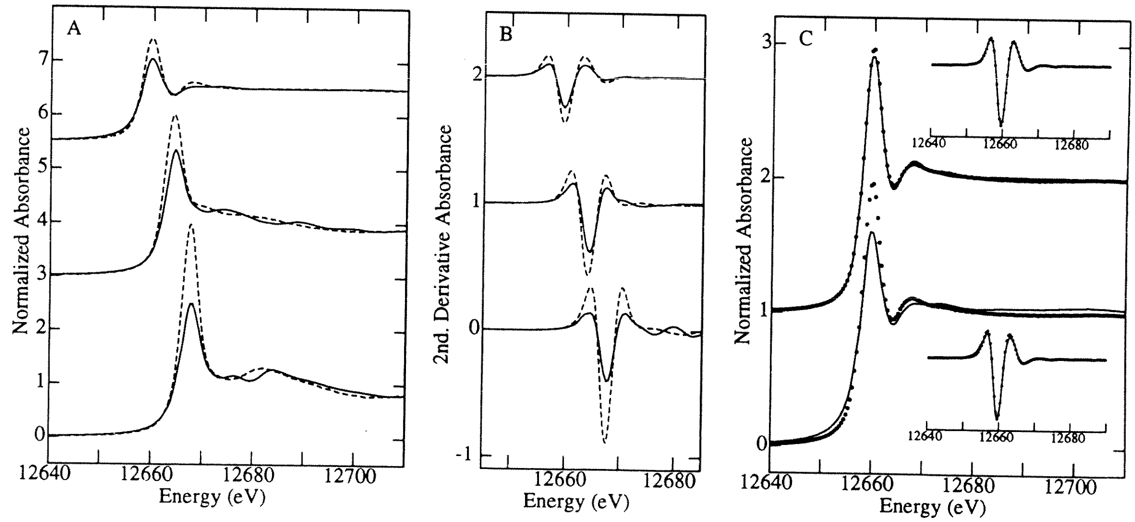

Fig. 2. Selenium K-edge absorption spectra of model compounds (data collected in transmission) and Kesterson Reservoir soil (fluorescence data). (A) shows Se K-edge absorption spectra and (B) shows corresponding second derivatives of model compounds. The model compounds were (top, solid) elemental Se (grey hexagonal), (top, dashed) elemental Se (red monclinic), (middle, solid) Na_2SeO_3 powder, (middle, dashed) SeO_3^{2-} (aq), (bottom, solid) Na_2SeO_4 (powder), and (bottom, dashed) SeO_4^{2-} (aq). (C) shows two fits to the 25-mm-depth Kesterson Reservoir soil sample, the top with red Se(0) and the bottom with gray Se(0). The dots show the points, and the solid line shows the fit. The results of these fits are shown in Table 1. It is clear that the best fit is obtained with the red form of Se. The inserts show the corresponding second derivative fits.

have been published previously (Pickering et al., 1995). It is clear from Fig. 2 that Se K-edge XAS is highly sensitive, not only to the valence state of Se but also to the specific local environment within a given valence state, and in the fits of the absorption edges (see below), it was possible to discriminate between these different forms of Se(IV) and Se(0) based on differences in fine structure. In particular, the fine structure above the first, strong transition is found to be especially diagnostic of the species present. Fitting unknown spectra to linear combinations of model compound K-edge spectra has previously been successfully applied in the case of S in various coal and petroleum samples (George and Gorbaty, 1989; Waldo et al., 1991; Karsai et al., 1994) and in oxidation of aqueous sulfides (Vairavamurthy et al., 1994).

Normalized K-edge absorption spectra for the Kesterson Reservoir soil samples revealed that Se is primarily in an elemental form (Pickering et al., 1994, 1995). Various linear combinations of standard Se spectra were tested for matching edge and second derivative spectra from the soil samples. The best fits were obtained largely from the spectrum of elemental (red monoclinic) Se. Example fits are shown in Fig. 2C for the 25-mm depth Kesterson Reservoir soil P4X. Here, two fits were attempted with either gray or red Se. It is clear from Fig. 2C that the superior fit is obtained with the red Se. This is also reflected in the goodness of fit parameter R in Table 1, which is at least an order or magnitude better for this fit. The sum of components parameter S for the derivative fit with the gray phase is found to be substantially different from unity, also indicating the inadequacies of this fit. For the 25-mm depth soil, the best-fit proportions for elemental Se based on edges and second derivatives were 97 and 94%, respectively. For the 100-mm depth sample, red monoclinic Se(0) comprised 86 and 84% of the total Se based on edge and second derivative fits, respectively (Table 1). The remainder of the fitting was optimized with minor contributions of the spectrum from Se(IV). Although some previous research on Kesterson Reservoir sediments also suggested the presence of elemental Se (Weres et al., 1989a; Tokunaga et al., 1991), this study is the first to provide direct spectroscopic evidence supportive of this interpretation. Since our original work (Pickering et al., 1994, 1995), XAS has also been used to show red Se to be the product of microbial metabolism of selenite from aqueous solution (Buchanan et al., 1995).

Table 1. K-edge and second derivative fits of Se in Kesterson Reservoir soils and in laboratory sediments. Se(0) is fitted as red, monoclinic elemental Se, except for the fit marked with *, for which hexagonal, gray Se is used. Se(IV) and Se(VI) are aqueous sodium selenite and selenate, respectively, for all fits. R is the R-factor, given by $R = 10^7 \times \Sigma(I_o - I_c)^2/N$, where I_o and I_c are the observed and calculated data points, respectively, and N is the number of points. S is the sum of the observed fractional contributions of all the components of the fit. This value should approach unity for a good fit. The accuracy of the percentage values is estimated to be ±5% (see Materials and Methods).

Sample	Fitting method	Se(0)	Se(IV)	Se(VI)	S	R
			%			
Kesterson P4X sed., 25 mm	K-edge	97	3	0	1.02	6.81
	2nd derivative	94	6	0	1.10	0.186
Kesterson P4X sed., 25 mm*	K-edge	100*	0	0	1.04	176
	2nd derivative	97*	3	0	1.63	1.20
Kesterson P4X sed., 100 mm	K-edge	86	14	0	0.998	56.0
	2nd derivative	84	16	0	1.21	2.43
Amended sediment, Day 0.2	K-edge	0	5	95	1.04	22.1
	2nd derivative	0	7	93	1.06	1.83
Amended sediment, Day 1.0	K-edge	0	35	65	1.03	13.1
	2nd derivative	0	36	64	1.04	0.621
Amended sediment, Day 3.7	K-edge	35	65	0	1.02	3.69
	2nd derivative	36	64	0	1.04	0.149
Amended sediment, Day 50	K-edge	100	0	0	1.01	1.04
	2nd derivative	100	0	0	1.03	0.25

Temporal changes in Se concentrations and speciation [Se(VI) and Se(IV) determined by HGAAS] in ponded waters from the laboratory columns are shown in Fig. 3A and 3B. Occasional comparisons with ICP analyses indicate that suspended Se(0) was not present in these waters. Values shown in these figures represent averages of analyses on upper and lower pond water samplings,

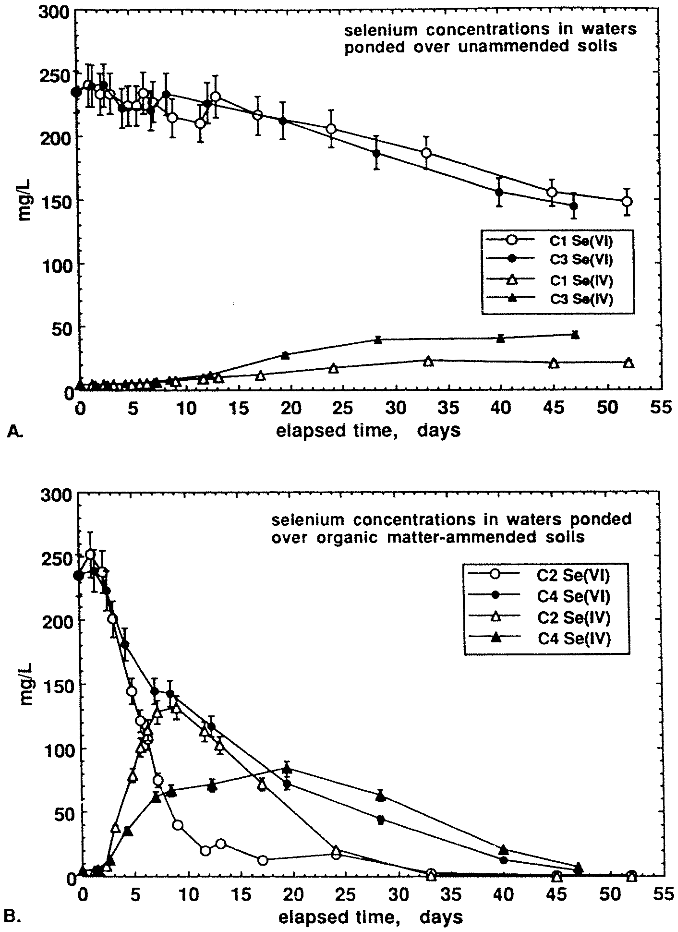

Fig. 3. Selenium concentrations in ponded waters, measured with hydride-generation atomic absorption spectrometry. (A) waters ponded over unamended soils, (B) waters ponded over soils amended with organic matter.

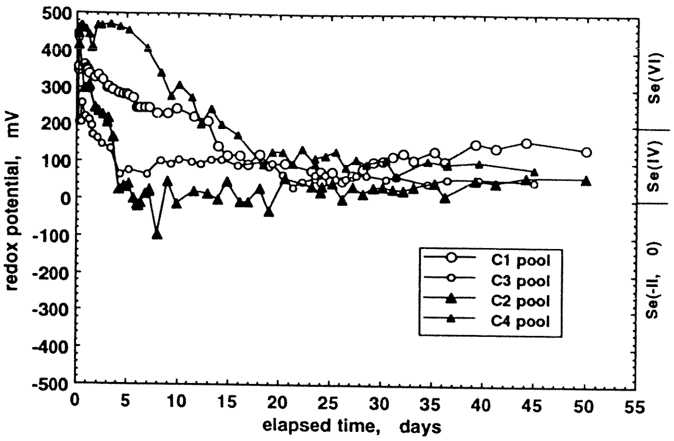

Fig. 4. Time trends of redox potential measurements in ponded waters. C1 and C3 are from waters ponded over unamended soils. C2 and C4 are from waters ponded over soils amended with organic matter.

although differences were nonsystematic and always <4%. Lack of measurable spatial gradients in either Se(VI) or Se(IV) within ponded waters, despite clear temporal changes, demonstrated that well-mixed conditions prevailed to within 10 mm or less of pool-sediment boundaries. Total Se concentrations in waters ponded over the unamended soils gradually decreased during the 48- to 51-d ponding period (Fig. 3A). At the end of this period, the aqueous Se concentration was still 75% of its original value. Conversion of some of the original Se(VI) to Se(IV) was observed in these surface water samples, with final Se(IV) fractions accounting for 12 to 25% of total dissolved Se. Volatilized Se amounted to <0.2% of the original Se in the ponded waters. Thus, 25% of the original surface water Se was transferred to the underlying sediment. Much greater decreases in total dissolved Se were observed in waters overlying sediments that were amended with additional organic matter (Fig. 3B). Rapid increases in the proportion of dissolved Se that occurs as Se(IV) are also evident in the data from waters ponded over organic matter amended soils. The maximum observed proportion of dissolved Se that is in the Se(IV) was as high as 86%. Final solution Se concentrations in this case ranged from 0 to 5% of original values. Volatilized Se amounted to <0.3% of the original Se in these ponded waters. Thus, at least 95% of the original surface water Se was transferred to the underlying, organic matter amended sediments.

Time trends in redox potential measurements in the ponded waters correlated roughly with Se reduction, as indicated in Fig. 4. In Fig. 4, approximate boundaries for stabilities of Se(VI), Se(IV), and Se(-II, 0) suggested in Masscheleyn et al. (1990) are indicated along the right edge. Quantitative relations between redox potentials and Se speciation were not established, presumably because of lack of equilibrium (Lindberg and Runnells, 1984; Runnells and Lindberg, 1990). This disequilibrium is illustrated in Fig. 5, where equilibrium Eh values calculated from measured pH (6.5 to 7.5) and Se(IV) and Se(VI) concentrations in pond waters [using relations provided in Elralshidi et al. (1987)] are compared with measured redox values. The diagonal line in Fig. 5 indicates ideal 1:1 correspondence between predictions and measurements.

Transport of Se from surface waters to surface sediments is reflected in the XRF-determined total Se profiles in both types of columns, as shown in Fig. 6A and 6B. Selenium concentrations in near-surface sediments are

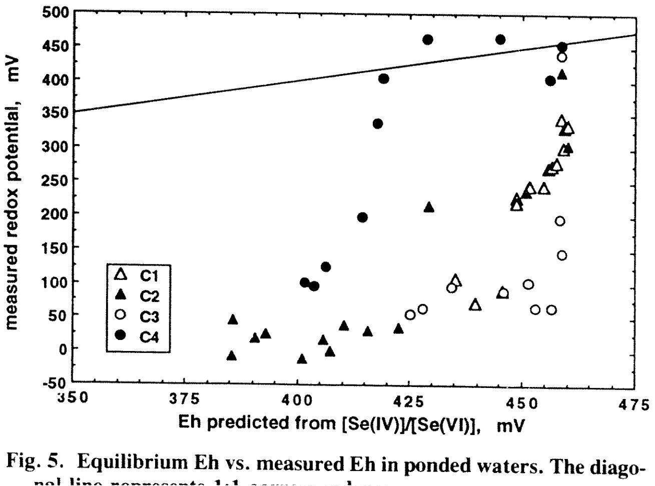

Fig. 5. Equilibrium Eh vs. measured Eh in ponded waters. The diagonal line represents 1:1 correspondence.

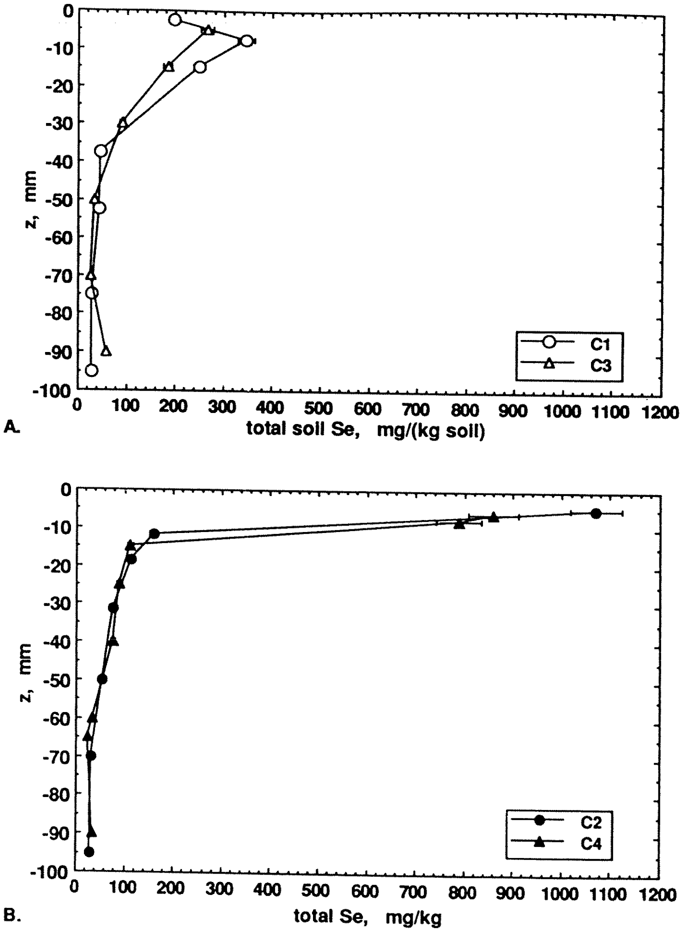

Fig. 6. Total Se concentration profiles in sediment columns, measured by x-ray fluorescence spectrometry. (A) columns unamended with organic matter, (B) columns amended with organic matter (Z = depth).

typically at least 10 times more than values deeper in the profile. Although samples for these total Se analyses were obtained following air drying of the soil columns, evaporative redistribution is not expected to be a significant influence on the final profile. This conclusion is based on XRF-measured profiles of Br in these dried samples, which showed a maximum possible evaporative enhancement of 30% at the surface relative to the bottom. The XAS results described later, which indicate the predominance of insoluble elemental Se, provide further support for this conclusion. The static ponding method used in this experiment introduces an important difference between the laboratory columns and the ponded sediments at Kesterson Reservoir. In these columns, advective transport of Se is essentially restricted to the initial ponding event. The minor volumes of pore waters collected from the soil water samplers amount to <5 mm of additional equivalent seepage. Thus, accumulation of Se within sediments after the initial flooding can only arise from diffusion or deposition from the ponded waters. Research currently in progress is addressing diffusive exchanges of Se(VI) and Se(IV) between the ponded waters and surface sediment pore waters. Preliminary results indicate that mass transfer models can be used to closely predict aqueous concentrations in one compartment based on measurements obtained in the other. On a much smaller scale, diffusion of Se(VI) in soil to reducing zones surrounding decomposing roots was observed with the synchrotron x-ray fluorescence microprobe (Tokunaga et al., 1994b).

Time trends for shallow sediment pore water Se concentrations (determined by HGAAS) are shown in Fig. 7A and 7B. The more rapid reduction of Se(VI) to Se(IV) and the more rapid decreases in solution phase Se concentrations in sediment vs. in the overlying waters is evident in both types of columns. The times to reduce the pool water Se(VI) concentrations to half of the original concentration in unamended systems are greater than the 52-d maximum ponding period (Fig. 3A), while this extent of reduction only takes ≈ 10 d in the sediments (Fig. 7A). In the amended systems, pool water Se(VI) concentrations are reduced to half the initial value by 5 and 12 d (C2 and C4, respectively), while the reduction within the shallow sediment occurs within 3 d (Fig. 7B). The deeper sampler within the C4 sediment exhibits Se(VI) concentrations and trends indicative of a series of dominant processes. The initial low concentrations of Se(VI) at this depth (80 mg L^{-1}) suggest that these pore waters initially comprise 34% applied seleniferous waters and 66% native soil water. Increases in Se(VI) concentrations during the first 8 d in these deeper pore waters probably result from diffusion from immediately overlying pore waters. Ultimately, Se(VI) reduction is also dominant in these deeper pore waters. Also, the influence of added organic matter in accelerating reduction rates is observed. Time trends in sediment redox potentials are shown in Fig. 8. Note that Eh values measured within sediments are typically lower than values observed in the ponded waters (Fig. 5), falling to levels associated with Se(0) and Se(-II). The persistence of measurable concentrations of Se(VI) and Se(IV) in sediment waters up to 20 d of ponding again suggests lack of redox equilibrium. However, the Pt electrodes embedded in sediments were not rechecked at the end of the experiment, leaving open the possibility of drifts in calibration. The lack of significant drift in calibrations for Pt electrodes placed in pool waters and at the sediment surface suggest that errors in the deeper sediment electrode readings were probably minor.

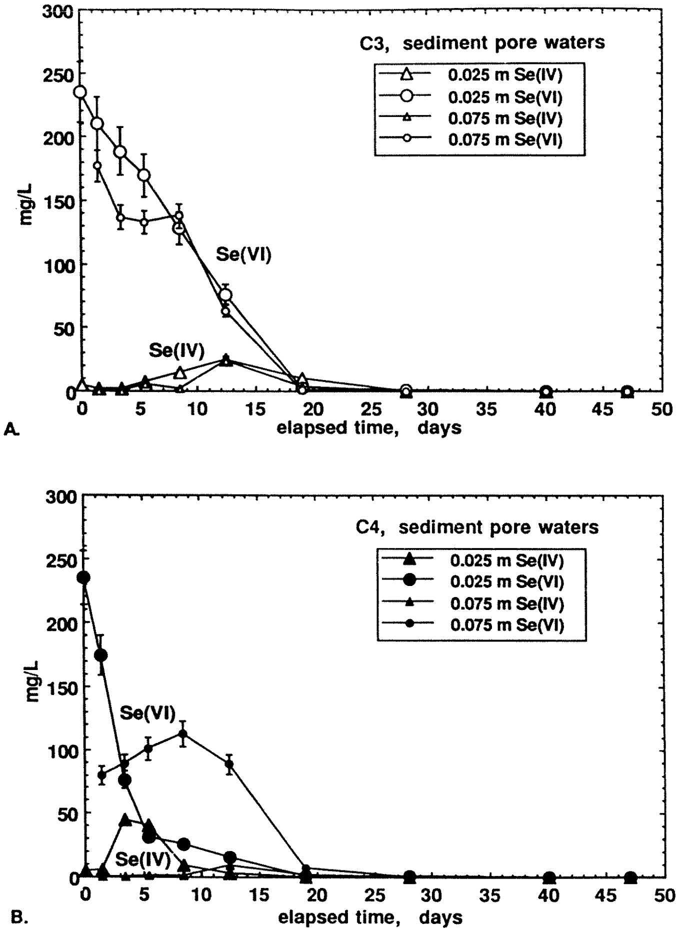

Fig. 7. Time trends for sediment pore water Se(VI) and Se(IV) concentrations, measured with hydride-generation atomic absorption spectrometry. (A) unamended sediment, (B) column with organic matter amendment added to the upper 30 mm of sediment.

The laboratory column sediment samples analyzed by XAS were obtained from the upper 0- to 25-mm interval. Samples of sediments that were amended with organic matter were analyzed after 0.2, 1.0, 3.7, and 50 d of ponding. The normalized Se K-edge absorption spectra of these samples, and their 2nd derivatives, fitted with model spectra are summarized in Table 1. The 0.2-d sample is essentially identical to that of the original Se solution supplied to these columns. By 1.0 d of ponding, ≈30% of the Se was reduced from Se(VI) to Se(IV). By Day 3.7, none of the original Se(VI) was detectable. The spectrum was transformed to one representing a combination of 65% Se(IV) and 35% Se(0). By Day 50, the amended sediment Se K-edge spectra were consistent with 100% red, monoclinic Se(0). For the columns that were not amended with organic matter, only sediment

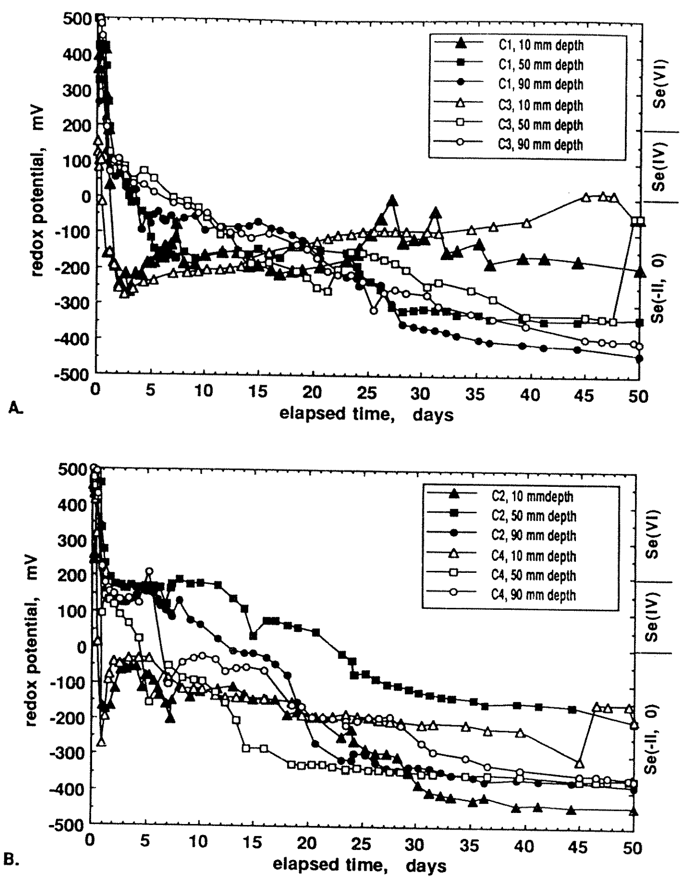

Fig. 8. Time trends in sediment Eh. (A) unamended sediment columns, (B) sediments amended with organic matter.

samples collected at the end of the experiment (≈ 50 d) were analyzed by XAS. These samples were also fit well with the spectrum of red elemental Se but exhibited some rapid reoxidation.

Sediments collected at the end of the experiment were tested for possible short-term Se reoxidation, 2 d after sampling. Differences in rates of reoxidation were also observed between the amended and unamended sediments. In the former, XAS of wet sediments stored in N_2, wet sediments stored in air, and similar samples that were air dried showed essentially no change to the spectrum of monoclinic Se. In contrast, spectra from the unamended sediment showed considerable oxidation in the aerated samples (Fig. 9). Reoxidation of Se in Kesterson Reservoir surface sediments progresses at much slower rates. Under variably moist, drought-dominated field conditions, Se reoxidation to Se(VI) at Kesterson Reservoir was estimated to occur at a first-order rate of ≈ 0.05 yr^{-1} (Tokunaga et al., 1994a; Benson et al., 1994). Recent laboratory experiments provide first-order reoxidation rates for Kesterson soil Se in the range of 0.058 to 2.4 yr^{-1} (P.T. Zawislanski and M. Zavarin, 1994, personal communication). Additional studies are needed to explain differences among observed reoxidation rates.

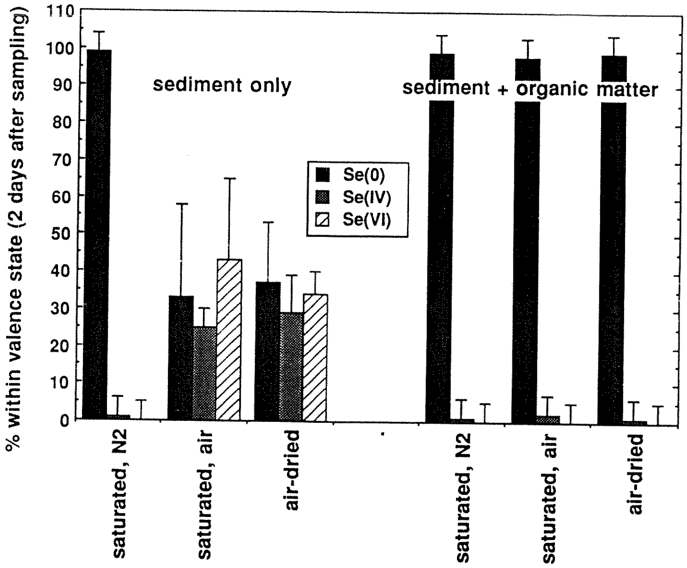

Fig. 9. Influence of short-term sample preservation on Se speciation in sediments ponded for 48 to 50 d. X-ray absorption spectrometry was performed 2 to 3 d after sediment sampling.

SUMMARY

This XAS study provided direct evidence for the presence of elemental Se in contaminated soils from the Kesterson Reservoir and in laboratory soil experiments designed to simulate possible reduction processes at Kesterson. Selenium in this reduced form is far less mobile than in more oxidized forms. Thus when present as Se(0), its transport through the soil profile and in groundwaters is strongly retarded. The reduction process can occur within a few days. The time-frame for reduction ultimately controls Se mobility and the extend of groundwater contamination. Reduction of Se to Se(0) also diminishes its bioavailability relative to more oxidized species as well as relative to common organic species, thus lessening the detrimental impact of this fraction of the Se inventory on wildlife. However, complete isolation of Se(0) from biota cannot be assumed in view of the recent study by Luoma et al. (1992). The rapid appearance of Se(IV) and Se(VI) in the unamended soils upon re-exposure to air also indicates that the rate of Se(0) reoxidation is not always slow. Information on the oxidation state of Se provided by XANES measurements complements information on Se concentrations obtained by conventional analysis techniques such as emission spectrometry and does not require elaborate extraction procedures that may alter the chemical form of Se. Although transformations of Se were the focus of this study, this work also provides an example of many potential applications of XAS in research on a wide variety of other elements in soils. This type of element-specific information is essential in understanding the basic chemistry, geochemical cycling, impacts, and management of environmental contaminants.

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